

Investigations of Bonding in Skutterudites by Electron Energy-Loss Spectroscopy

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ABSTRACT

The local electronic structure of phosphorus in the binary skutterudites CoP₃ and NiP₃, and in the filled skutterudite LaFe₄P₁₂ are studied using a combination of electron energy-loss spectroscopy and *ab initio* calculations. Relative to CoP₃ we observe a filling of phosphorus s and d states in NiP₃, while for LaFe₄P₁₂ increased EELS intensity indicates more empty s and d states close to the Fermi-level.

INTRODUCTION

In a transmission electron microscope (TEM), minute amounts of material can be investigated using a variety of techniques. Electron diffraction allows detailed studies of the crystal structure of nanosized volumes, direct imaging gives information on structural domains and the ordering of grain boundaries, while detection of characteristic x-ray radiation allows elemental quantification. In this contribution, we employ electron energy-loss spectroscopy (EELS) in a TEM [1] together with theoretical calculations using the real space multiple scattering approach to study the electronic structure and bonding of several materials with the skutterudite structure.

While these materials have received extensive attention due to their thermoelectric properties, there have been fewer experimental studies of their bonding characteristics. Anno et al. [2] and Grosvenor et al. [3, 4] used x-ray photoelectron spectroscopy (XPS) to explore the occupied density of states (DOS) in order deduce charge transfer effects, while Diplas et al. [5] combined XPS and analysis of the x-ray induced Auger electrons to investigate the ionic character of the bonding in CoP₃. While these studies focus on the occupied DOS, EELS allows the investigation of the unoccupied states near the Fermi-level, thereby giving a complementary picture of the bonding effects.

This approach was recently used to investigate the 3d occupancy of transition metal atoms in skutterudites [6], while the present study focuses on the local density of states of phosphorus in the CoP₃, NiP₃ and LaFe₄P₁₂ skutterudites [7].

EXPERIMENTAL AND THEORETICAL PROCEDURES

In EELS, an incident (primary) high energy electron transfers some energy to the sample, and excites one of the constituent electrons into a higher energy state [1]. For the excitation

process to occur, the electron must receive an energy $E \geq E_f - E_i$, where E_f is the Fermi-energy and E_i is the initial binding energy. After the primary electron has transferred energy, it leaves the sample and enters a spectrometer where its energy is measured, and the amount of energy loss is deduced. In a single electron approximation, the measured energy-loss intensity $I(E)$ is given by [8]:

$$I(E) \propto \rho(E_i + E) |\langle \Psi_f | e^{ik \cdot r} | \Psi_i \rangle|^2 \quad (1)$$

where $\rho(E_i + E)$ is the DOS at an energy E above the initial state binding energy, and $|\langle \Psi_f | e^{ik \cdot r} | \Psi_i \rangle|$ is a matrix element describing the amount of spatial overlap between the initial and final states. This matrix element ensures that it is the *local* density of states (IDOS) that is probed, and investigations of elemental specific energy loss edges therefore gives information on the local arrangement of electrons in the material. It should also be noted that the dipole selected transitions dominate the spectrum, and the dipole selection rule is usually considered valid. The DOS term in equation 1 above therefore becomes a site- and symmetry-selected density of states, giving detailed information on the electronic structure of the material studied.

An important caveat to this interpretation is the problem of excited states. In spectroscopy one explicitly studies the material in an excited state. In the case of EELS, one of the core electrons are removed from its ground state and transferred to a higher energy state. As a consequence, the density of states probed in EELS is not the ground state DOS, but rather the DOS in the presence of a core hole. Direct comparisons with the density of states conventionally calculated by ground state methods such as density functional theory will therefore not be accurate. In stead, the calculations must be explicitly performed on models of the system in the excited state [9].

In this work we use the real space multiple scattering approach [10] where the spectrum is modeled by considering the excited electron as an outgoing wave which is scattered by the potentials due to the surrounding atoms and the electron distribution. More specifically we use the FEFF8.5 code [11, 12] to construct self consistent potentials including the core hole from a cluster of approximately 45 atoms, which are then used in full multiple scattering calculations of the spectrum in a cluster of about 150 atoms. The experiments were performed in a JEOL 2010F TEM fitted with a Gatan GIF 200 EELS spectrometer. The energy resolution obtained was approximately 1.2 eV as measured by the full width at half maximum of the zero loss peak.

RESULTS AND DISCUSSION

Figure 1 shows the experimental and theoretical $L_{2,3}$ edges of the three skutterudites. While the overall shape of the three edges are rather similar, there are important differences that should be noted. Of particular importance are the features close to the edge onset, which reflect the DOS close to the Fermi-level. This is the region which is most heavily influenced by bonding and charge transfer.

While CoP_3 displays a visible peak just above the onset (indicated), this feature is reduced in NiP_3 , indicating a filling of phosphorus s and d states in this compound compared to the situation in CoP_3 . In the filled skutterudite, $\text{LaFe}_4\text{P}_{12}$, the situation is different, with the initial edge showing a significant increase in intensity compared to both CoP_3 and NiP_3 .

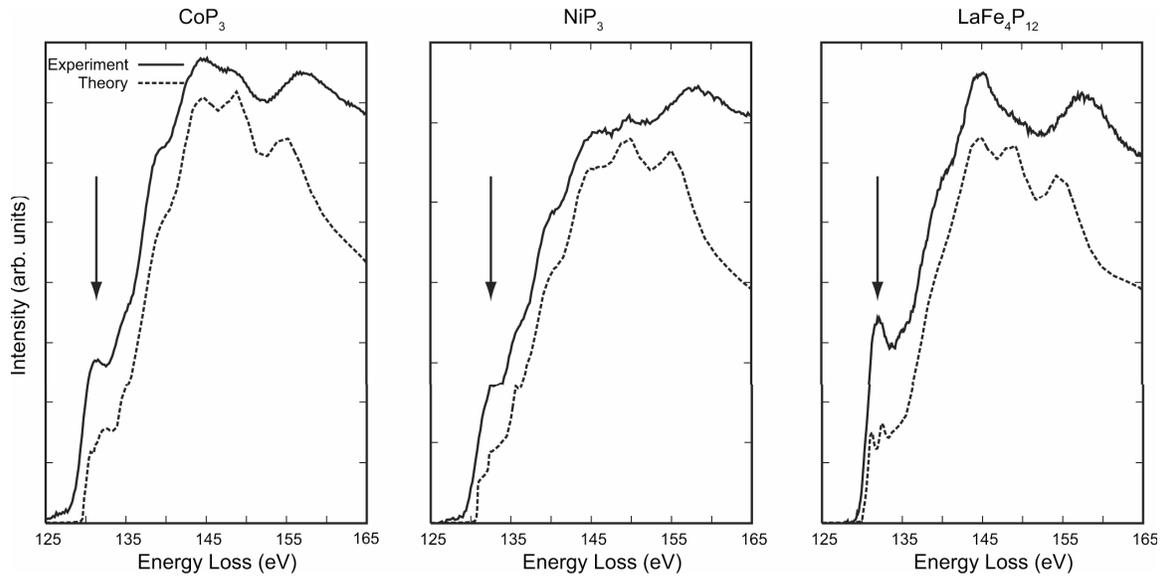


Figure 1: Experimental and theoretical EELS spectra of the phosphorus $L_{2,3}$ edges in CoP_3 , NiP_3 , and $\text{LaFe}_4\text{P}_{12}$.

The calculated $L_{2,3}$ edges are shown together with the experimental results. The theoretical calculations successfully reproduce and confirm the main features of the edge up about 155 eV, including the intensity variations of the initial peak. Above 155 eV the correspondence is not as good.

From simple considerations using the Dudkin model [13] these variations should be expected. In the standard skutterudites with a column 9 transition metal, e.g. CoP_3 , the bonding is usually considered covalent, with both the metal and pnictogen contributing electrons toward hybridized d^2sp^3 bonds. In NiP_3 , however, the transition metal atom has one electron more. This causes a suppression the initial peak observed in figure 1, either through explicit transfer of charge from Ni to P, or through a reduced need for P to donate electrons towards bonding. In the filled skutterudite, however, we observe an increased intensity of the initial peak. In this material, Fe has been substituted for Co, and La filled in the vacant 2a positions in the unit cell. Iron has one electron less than cobalt, and so the binary skutterudite with composition FeP_3 does not form. There are not enough electrons to saturate the octahedral bonds as in CoP_3 . In the filled skutterudite, however, the needed electrons are supplied by lanthanum in a 3+ state. However, this only supplies three out of the missing four electrons, which necessitates an increased contribution by the phosphorus atom and causes an large number of empty states just above the Fermi-level as observed in figure 1 [7].

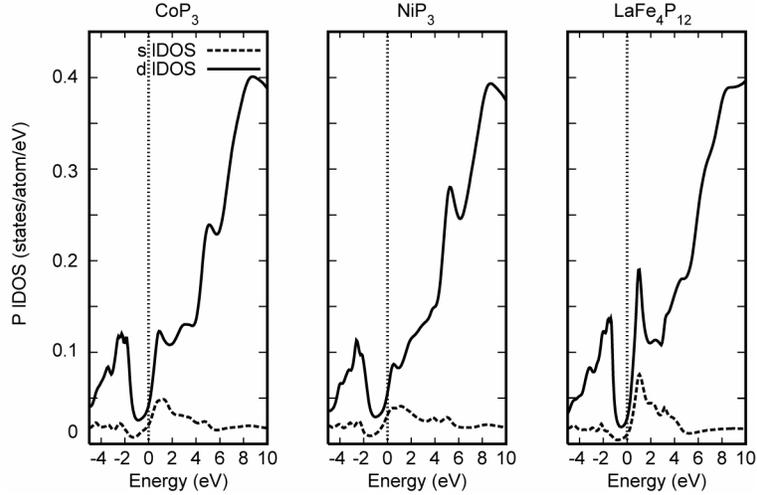


Figure 2: The s and d projected local density of states of phosphorus in CoP_3 , NiP_3 , and $\text{LaFe}_4\text{P}_{12}$. The DOS plotted here is that of the excited phosphorus atom.

The observed intensity variations can also be understood from differences in the IDOS of the three materials close to the Fermi-level. Figure 2 shows the s and d projected IDOS of phosphorus calculated using the FEFF package. While CoP_3 shows a definite peak in the DOS just above the Fermi-level, this feature is suppressed and partially located below E_f in NiP_3 . Meanwhile $\text{LaFe}_4\text{P}_{12}$ exhibits a very sharp peak in the available number of states just above E_f . These features are directly related to the observed intensity variations in figure 1, and signal differences in the binding characteristics between these materials. Although the calculated density of states indicates that most of the observed intensity in the initial peak comes from transitions to empty d states, there is also a significant contribution from transitions to empty s states.

CONCLUSION

Using electron energy-loss spectroscopy and real space multiple scattering calculations, we have investigated the electronic structure of the three phosphorus based skutterudites CoP_3 , NiP_3 , and $\text{LaFe}_4\text{P}_{12}$. Our investigations indicate a reduced number of empty phosphorus s and d states in NiP_3 compared to the situation in CoP_3 , possibly due to the increased number of valence electrons provided by the substitution of Ni for Co. Meanwhile, in $\text{LaFe}_4\text{P}_{12}$ the number of electrons from the transition metal contributing to bonding is reduced and not fully compensated by the presence of the La^{3+} ions, causing a larger number of empty phosphorus s and d states close to the Fermi-level.

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